

**DEGRADATION OF LEAD (Pb) FROM CAR WASH WASTE WATER SAMPLE
USING ULTRASONIC ASSISTED EXTRACTION PROCESS**

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ABSTRACT

The waste water from the car wash industry is actually containing heavy metals that will affect environment and health. Many researchers have done different ways to degrade heavy metal in the different sources of waste water. In this study, lead (Pb) is the major heavy metal found from the car wash effluent sample. The degradations of this heavy metal use the ultrasonic process which is assisted by the extracting solvent for get higher degradation. Then, the aim of this study was to find the suitable condition of degradation lead (Pb) from car wash waste water with focused on the influence of time sonication, volume solvent and type of the solvents used. Two types of solvent are used in this research which are methanol and acid hydrochloric. Each solvent was mixed with the sample with different volume also the time process. The two condition of treatment was done; by present and absent of ultrasonic treatment. The analysis of sample was using Atomic Absorption Spectrophotometry (AAS) to identify the final lead (Pb) concentration. Result found that the suitable conditions for lead (Pb) degradation were using 3 minutes ultrasonic process and assisted with methanol (MeOH) solvent by the volume 10ml. It was shown that, the higher percentage degradation was achieved by 42.5%. In conclusion, Ultrasound alone was not good enough to degrade the heavy metal itself in waste sample and by an addition of solvent, it was played a role as predominated over that of ultrasonic process enhanced the result performance. The standard condition of process was important to recognize for further commercialized programs.

ABSTRAK

Kandungan logam berat daripada sisa air stesen mencuci kereta sebenarnya akan memberi kesan kepada persekitaran dan juga kesihatan. Terdapat ramai pengkaji yang telah menggunakan pelbagai cara untuk menguraikan logam berat daripada pelbagai sumber sisa air. Di dalam kajian ini, plumbum (Pb) telah dijumpai di dalam sampel sisa air mencuci kereta sebagai logam berat yang utama. Proses penguraian di dalam kajian ini adalah menggunakan proses Ultrasonik dibantu dengan kehadiran larutan ekstrak untuk meningkatkan lagi penguraian logam berat di dalam sampel. Oleh itu, objektif daripada kajian ini adalah untuk menentukan keadaan yang sesuai dalam melakukan penguraian kandungan plumbum (Pb) di dalam sisa air daripada stesen mencuci kereta dengan memfokuskan kajian kepada kesan perubahan masa rawatan ultrasonik, isipadu larutan ekstrak dan jenis larutan ekstrak yang digunakan. Dua jenis larutan ekstrak digunakan iaitu metanol dan hidroklorik asid dengan setiap larutan ekstrak akan dicampurkan bersama sampel dengan isipadu larutan ekstrak dan masa rawatan yang berbeza. Sebagai tambahan kajian, keadaan rawatan sampel juga dilakukan dalam kehadiran rawatan ultrasonik dan juga ketiadaan rawatan ultrasonik. Analisis daripada kajian ini dilakukan dengan menggunakan 'Atomic Absorption Spectrophotometry (AAS)' bagi menentukan kepekatan plumbum (Pb) pada akhir rawatan. Keputusan menunjukkan keadaan yang sesuai untuk menguraikan kandungan plumbum (Pb) adalah dengan kehadiran rawatan ultrasonik selama 3 minit bersama larutan ekstrak methanol (MeOH) sebanyak 10ml isipadu larutan. Peratusan penguraian yang tinggi telah diperolehi daripada kajian ini adalah sebanyak 42.5%. Kesimpulannya, rawatan Ultrasonik dapat ditingkatkan lagi keberkesanannya dengan kehadiran larutan ekstrak dalam penguraian logam berat daripada sisa air sampel dan seterusnya memberikan peratusan penguraian yang tinggi. Penentuan keadaan proses hendaklah bersesuaian dengan rawatan bagi membolehkan cara ini dikomersilkan kelak.

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LIST OF ABBREVIATIONS

ppm	-	Part per million
rpm	-	Revolutions per minutes
%	-	Percent
ml	-	Milliliter
MHz	-	Megahertz
kHz	-	Kilohertz
V	-	Voltage
pH	-	Acidity or alkalinity measurement
°C	-	Degree Celsius
Min	-	Minute
cm	-	Centimeter
W	-	Watt

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CHAPTER 1

INTRODUCTION

1.1 Background of Study.

In our world environment, mainly contain three serious of pollutions; air, soil and water. However, water is nowadays as critical thing being polluted. In China, the industrial park those have increasing in manufacturing factory such as Printed Circuit Board (PCB) made great impact of heavy metal pollution in the water effluent that undergo to environmental pollution (C. Li et al., 2009). In several years, other industry sector like car wash also increasing developed which is to fulfill the higher demands of consumer in lack of time then want to get good service and result for their car.

Nowadays, car wash sectors majority only discharge their waste water without the treatment. Car wash sector mainly the raw material is detergent or soap and wax. Both actually containing hazardous properties at the same poisoning which affect our environment and us own especially person that in charge with car wash activity. The production of bubble from the detergent is perform less surface tension on the surface vehicles and make it easy to remove any dirt or soils. Based on the Community Eco-Partner Rock Bay reported, the waste formation actually has summations of oil, grease, mud or other which is as major water pollution come from the automotive industry. Even detergent or foam makes our car shining, on other hand they bring us pollution.

The associated of effluent car was with pollutants like engine oil residues, sediments and detergent will bring harmful to the environment and health. Furthermore, the pollutants also containing heavy metal that will be reacting for other formation hazardous compound. Based on the Material Safety Data Sheet (MSDS) of Cellinite Biotabs from Cellinite Technologies, Inc. the ingredient composition of detergent was containing higher sodium (Na) compound and biologically active surfactant. Then, the major known emissions sources for car wash represent Cadmium (Cd) which was founded in Stockholm City state sample (B. Bergback et al., 2000). In the H.A. Tayim and A.H. Al-Yazouri (2005) had report that the industrial waste water from the soap and detergent manufacturing from Emirate of Abu Dhabi, United Arab Emirate local was containing heavy metal such as iron (Fe), zinc (Zn), lead (Pb), Copper (Cu) and Manganese (Mn). This was analyzed by using the ICP-OES for initial concentration determination for sample preparation. Here, the removal of heavy metal was founded but not suitable to perform investigated because of lack of heavy metal sources in the waste water samples. The lack sources of heavy metal overcome with the problem difficult to trace changes concentration before and after the treatment process done for the waste water. Initial concentration is the main point for making analysis and also comparison.

Furthermore discovered by J. L. William (2000) founded that the particular heavy metals in car wash effluent were Pb, Fe, Cu, Cadmium (Cd) and Barium (Ba). Normally, the effluent car wash are varied in concentration of heavy metal because affect of the raw material dilution and also the washing condition activity. It will show that different places of effluent taken got different range of concentration heavy metal. In this research, the sample was taken from the Gambang station Car Wash which is one of the desired car wash of the consumer in Gambang citizen.

Recently, the accumulation and transport of heavy metal in soils, air and water has become a hot topic to discuss in many researches. Environment legislature has mentioned that the increasing heavy metal in water especially will disturb aquatic population with help in production of algae. These phenomena will affect the biochemical oxygen demand (BOD) aquatic life itself (M. A. Ogundiran et al., 2010 & M. Gholami et al., 2010). Other than that, heavy metal can affect human by several routes which are vaporization, inhaling and ingested in food. Lead exposure can cause health problems like renal failure, coma and ranging convulsions. The toxicity of metal which is high enough level was possible to risk the fetus development for pregnant women (Micheal M., 2002). Sodium normally used as common salt which also necessary for human. However, the higher concentration of sodium in body will damage our body.

Furthermore, the contacts of sodium with water were causes sodium hydroxide formation fumes. The formations were affecting our inhalation (throat) and can irritating skin, eyes and nose. This may cause sneezing and coughing then may result in difficult breathing and chemical bronchitis. Contact with eyes may result in permanent damaged and loss of sight (S. Charles and K. B. Karlyn, 2003). In addition, Zinc is also one of the important elements in the male body and its deficiency were causes anemia and retardation of growth and development. Based on its toxicity, zinc is perform as same as lead affects. In the excess of the toxicity of zinc will lead to causes impairment of growth and reproduction (J.O. Duruibe et al., 2007). So, each heavy metal will cause unwanted damaged when in higher concentration. The prevention steps need to be taken to prevent all the affect can settle down early.

Beside to prevent harmful heavy metal overcome our environment and health, the waste water treatment also can help in reducing clean water used. Sewage treatment plants an example treatment actually contributed 90% of water economized and can reduce the detergent consumption for car wash station by circulating water providing. This make researcher studied several methods that have been used for degrade heavy metal from the waste water which is including physical, chemical and biological process for improve the quality industrial water effluent. Containing several methods applied which is based on oxidation, microbiological, electrochemical decomposition and also photo decomposition process. Microbiological methods actually got an extra advantage

on the environment sector to be applied as a waste water treatment. However, when handling with life organism in process makes the parameter controlled is difficult and taken time to be settled. The preparation for the treatment also needs higher selectivity parameters to perform good performance. Chemical processes are designed to perform by means of chemical reactions. Here, base on the statement of Economic and Social Commission for Western Asia in 2003, chemical processes have the advantages than physical operations because of the additives available that react in the process.

In addition, removal heavy metal can also do by using activated carbon applications. Activated carbon is used as the catalyst that catalyzed the reaction of process of adsorption heavy metal. These process also affected by the characteristics of the activated carbon and optimum performance achieved by increasing the surface functional group on its. These needed higher cost and supervision during the process because activated carbon was sensitive selectivity (C. K. Ahn et al., 2009). The other adsorption methods were by natural zeolites which more effective in removal of cationic heavy metal species only (E. Erdem et al., 2004). In other specification, zeolites were undergoing complicated steps to be prepared and the cost of zeolites also higher for the process used. Ultrasonic process actually also widely used as one of the technique for removal of heavy metal (M. Olvera et al., 2008). Based on the review, because of the advantages of additives properties and effective of ultrasonic emulsification in removal treatment this thesis was come out with both of the efficient method combination.

In this research, extracting solvents based on acid and alcohol properties were used to assist with the ultrasonic irradiation process. These process was used instead other process because of: (1) Energy consumption. Ultrasonic process was needs lower energy and smaller volume chemical solvent than microwave extraction as a comparison. (2) Better time consumption than microwave extraction or distillation process to make analysis and adjustment of treatment condition. (3) Economic field. This process is less economic than adsorption processes which need high cost for properties preparation like need to perform calcinations of activated carbon with high temperature.

1.2 Problem Statement.

Waste water quality was categorized based on its physical, chemical and biological characteristics (Micheal M., 2002). Detergent properties like car detergent are containing several heavy metals which characterize under chemical parameters that will affect the environment condition. Furthermore, other addition of dirt would be also containing heavy metal that would also dilute in the car wash waste water. For example, lead (Pb) also can causes central nervous system damage after reach the toxicity level. At lower doses, it can cause anemia and kidney damage (A. Hites, 2007).

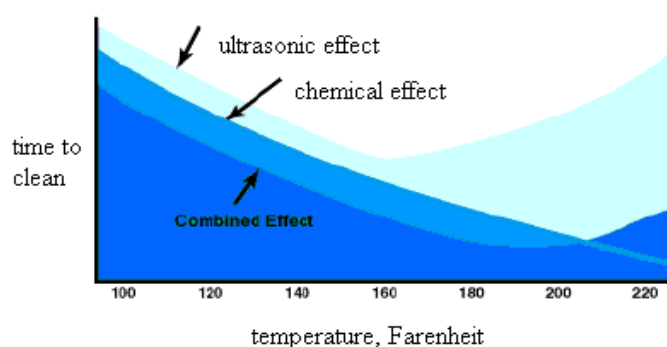


Figure 1.1: Comparison of methods treatment in degradation of heavy metal (F. J. Fuchs, 2002).

Figure 1.1 was illustrated that the efficiency of degradation heavy metal when the ultrasonic was combined with the chemical. As known, the sequence in extraction process containing extractable and exchangeable the heavy metal component because of the ionic properties which were affect the mobility also the reaction with another ionic compound to formed molecule by suitable addition solvent (J.-F. Peng et al., 2009).

In addition, the use of ultrasonic treatment in degradation or extraction treatment process has been drawn attention from some researcher because of the less time consumption and easier to monitor also handle the parameters condition during the treatment. Maintenance and supervision also less needed for the ultrasonic operation. Nevertheless, use of extracting solvent assisted of the solvents treatment can perform in the optimum condition with unaffected the environment and the properties of parameter

treatment waste water indeed. Sample of these researched was taken from car wash waste water and used to remove heavy metal which lead and zinc had been more efficiently by using Ultrasonic-assisted Extraction (UAE) process. So, these researched actually was sufficiently done due to the properties of sample itself and also the environmental issues to recover.

1.3 Objectives of Study.

The main objective of this researched is to find the suitable condition in degrading of heavy metal (lead, Pb) from car wash wastewater by using Ultrasonic-assisted Extraction (UAE) process.

1.4 Scope of Study.

Several conditions are manipulated in this research to achieve the objective, which is:

- (i) Using the different types of solvent for degrade lead (Pb); methanol and hydrochloric acid.
- (ii) Study and compare different composition volume of solvents effect in degree of degradation heavy metal at 5ml, 10ml and 15ml.
- (iii) Study of effect using different sonication contact time.

1.5 Research Contribution.

The rationales of this research done are:

- (i) To improve the quality of waste water effluent from car wash sector from any hazardous heavy metal into the environment which is will conducted to water pollution.
- (ii) To reduce the cost of waste water treatment. Coagulation process that normally used in waste treatment need addition of chemical which same steps that these researches done. However, Economic and Social Commission for Western Asia, 2003 was state that the coagulation process need longer time period and large area also facilities for sedimentation and settling of chemical.
- (iii) Contribute in the waste water treatment technology by suitable condition process used

CHAPTER 2

LITERATURE REVIEW

2.1 Car Wash Wastewater.

2.1.1 Physical properties.

Wastewater or dirty water from the car wash normally will contain detergent and soaps, grease and gasoline, and other residue from exhaust fumes. In addition, some sludge or muds attach on the vehicles also washes off. Heavy metal usually has the greater density than $4\text{-}5\text{gcm}^{-3}$ which performs it present from various human activities such as refining, mining and electroplating industries (K. W. Lawrence, 2009). The heavy metal normally dissolved in the form of solution and cannot be seen with normal eyes.

2.1.2 Chemical Properties.

Normally, car wash water discharge containing heavy metals or other contaminants. As an example, detergents can seriously affect the water quality because containing some pollutants such as; phosphate, sodium, potassium and other contaminants. Detergents can have toxic effect on a wide variety of marine life. That is why detergent must have their certain measurement to use even the biodegradable ones. Furthermore, from grease oil car it contains higher concentration of lead. So, based on this research, we can remove heavy metal that contained in water effluent to provide less hazardous of wastewater.

2.2 Heavy Metal Removal.

Heavy metal is a most important pollutant that affects our life and ecosystem. Several techniques done before in order to remove heavy metal from the wastewater discharged. Various treatments have been done such as chemical precipitation, flotation, ion exchange and also membrane filtration (K. W. Lawarence, 2009).

Basic concept of heavy metal removal is by the ion exchangeable either an atom or molecule that has lost or gained an electron from solution which is needed an electrical charge by performing in reversible chemical reaction. This reaction need immobile ion in the solution either naturally occurring or synthetically produces. Ion-exchange column is one of the equipment that used for remove heavy metal ions. A. Stoktosa and A. Wojtowicz (2002) found that, by using ion-exchange column several parameters is affect the process: sorption capacity of exchanger, volume solution till the moment of column breakthrough (V_{\max}) and column dynamics. Three heavy metal (Zn, Cd and Pd) is carried out to show efficiently removed from model solution by classified it as 1st class cleanness water. They found that, the ion column effluents gradually increase with various values of V_{\max} . This shown that, ion exchange process is affected by ion-exchange capacity which is actually depending on sorption capacity or amount of solute taken up for each metal. Using ion-exchange column sorption capacity for Pb is higher rather than Zn and Cd and this treatment can efficiency remove harmful heavy metal especially Pb from waste water as raw material.

2.2.1 Catalysis extraction.

M.D Loizidou and V.J Inglezakis (2007) was studied that, the possibility of ion exchange of heavy metal ions using polar organic solvents and natural zeolite clinoptilolite is approached. Heavy metal was studied is Cu, Cr and Fe with using solvent ethanol and acetone with the comparison result with deionized water. Result shown that, level of reaction of ion in water are much greater for Fe^{3+} (53.1%) in comparison to ethanol (12.5%) and acetone (3.1%), Cr^{3+} is exchanged in satisfactory levels in ethanol (46.8 and 27.4% respectively) and Cu^{2+} in acetone (23.8 and 26.6% respectively). Infrared (IR) and ultraviolet/visible (UV-Vis) spectrometry showed that complexes are formed, which are different in each solvent. So, the formation of precipitation, free

cations and pore zeolite opening will give affect for ion exchange occur for using different solvents extractor. Finally, the ion exchange of metals using zeolites is possible to take place in polar organic solvents and one significant finding is that selectivity can be totally changed. The structure containing various pore size of zeolites was make up the researcher find the other optimization structure that used for extraction by using zeolites. Furthermore, the zeolites price was expensive to use as extraction medium of waste water treatment. Cost is the main factor that needs to be considered to perform any management process.

2.2.2 Solvent Extraction.

Ultrasonic assisted extraction using acid solvent nowadays widely used to remove heavy metal in the waste water. This removal based on the high intensity formed from the ultrasonic agitation that affected from the different parameters that to the liquids sample. The important of solvent properties is boiling point and polarity. Polarity is the ability of solvents to reduce the electric field with performs chemical reaction of ion exchange and pH affect. Based on the previous study, EDTA and HCl is the efficient solvent to remove heavy metal in the contaminated soil. The breakdown of particle size speed up the extraction of heavy metal with less consumption of time rather than using natural treatment by producing powerful intimate of chemical and physical reaction process (J.S. Park et al., 2007). Based on this study, ultrasonic irradiation used at 20 kHz with power range 0~100 W with using ultrasonic horn diameter 2-cm and length 18-cm. The bottom horn was immersed 0.5 cm beneath the surface of sample solution. Ultrasonic power of 10 to 40 W was applied for up 12 minute. Here, analyzed shown that for the sonication time indicated the amount of efficiency extraction rate included with the solvent extraction of acid properties of EDTA. Residual fraction in heavy metal was 40% for Pb and Zn, 60% for Cu and 75% for Cd. Pb was the highest among these metals which indicates that Pb could be extracted more simply than other metals using acidic solvent properties.

In addition, based on the studied of Ultrasonic Extraction and Determination of Cyanuric acid in Pet Food, methanol was found to be the best one of the extraction solvent due to strong polarity of cyanuric acid and the interferences with solvent in the pet food. Ultrasonic is formed in an ultrasonic bath with 0.5g of spiked pet food in 25ml conical flask, followed by the addition of 20.0mL methanol as the extraction solvent.

The extraction process was conducted for 20 min of ultrasonication at room temperature and at the end the sample is centrifuged at 14000rpm for 5 min followed by filtered process. Selection of solvent extraction of cyanuric acid from the pet food is used four solvent and the extraction efficiency was increased in order acetonitrile < acetone < ethanol < methanol with their polarity sequence coordinate (C. Yu et. al, 2009). In the first 5 min nearly 75% extraction achieved and for the last 25 minute, about 97% of cynuric acid was extracted rather than 240 minutes required in the magnetic stirring extraction. Based on the researched founded that methanol was selected as extracting solvent because of the polarity substance of cyanuric acid and furthermore, time for ultrasonic extraction process also less than using other solvent which higher than 30 minutes for the optimization of degradation. The increasing time of process only increased energy cost and also more time consumption.

2.2.3 Chemical Precipitation.

Precipitation was due with formation of a solid in a solution during a chemical reaction which is in liquid form reaction. The formation is related with the nucleation onset process with consider the distinct thermodynamic phase. Some of an example phase may form via nucleation in liquid is crystals. Sonocrystallization is the ultrasound power that used to control the crystallization process. Here, ultrasound was used to influence the nucleation process and further control the crystallization with creates cavitation event to nuclei form new crystals and growth (A. Saikia et al., 2007). This researched reviews that, ultrasonic affected the precipitation or crystallization of hexanitrohexaazaisowurtzitane (CL-20) one of the high energy materials (HEMs) by perform fine particles uniform crystalline with desired morphology without any agglomeration compare with unsonicated sample. The researched was done by made comparison between sonicated and unsonicated sample with the analysis was by the Scanning electron Microscope (SEM). The time of sonicated process also studied between 5 – 17 minutes. The optimum condition with 95% against 90% precipitation occur resulted by more addition of heptane fraction to ethyl acetate solution with one fourth from 1 hour to only 15 minute. The ultrasonic treatment was helped in the process of crystallization CL-20 with produce desired morphology and precipitation of heptane with less of time needed. This researched succeed shown that ultrasonic was powerful equipment for reduced the time process.

2.2.4 Emulsification process

Emulsification liquid membrane (ELM) is one of the methods used to investigate the removal of heavy metal. In ELM process, the efficiency is determining based on the contact area and the size of the dispersed drops of the liquid membrane. These factors enhance with emulsification preparation condition to perform effective contacted and stable mixtures by supplying energy (Mahdi C. et al., 2010). The work was done by prepared the organic membrane is dissolved the bis(2-ethylhexyl)phosphoric acid(D2EHPA) and the hydrophobic surfactant sorbitan monooleate(Span 80) in hexane(diluents) and the internal phase consisted of an aqueous solution of sulfuric acid. Water-in-oil (W/O) emulsion was made by slowly adding the internal phase to the organic membrane phase upon intensive emulsification with the ultrasonic probe. All experiments were carried out at constant temperature ($25\pm1^{\circ}\text{C}$) using water jacket around the vessel, volume of stable emulsification(20ml) was dispersed in the feed phase (100ml of aqueous solution) and run in glass vessel 61mm diameter with four-paddle impeller of 20mm diameter. Then, the influence of operational conditions on the extraction efficiency is analysis using Atomic Absorption Spectrometry (AAS).

Furthermore, the process was conducted in several parameters affected which are will be discussed further in the next topic of this paper researched. Ultrasound conducted in emulsification and recovery copper (II) from waste water using water-in-oil (W/O) membrane process resulted that excess energy was performed emulsification for new interface formation and affect the cuprum (II) extraction by higher lifetime of external aqueous (W/O) phase to membrane phase.

With higher lifetime, extraction process by membrane performs more efficiently. Normally, membrane is used to remove inorganic contaminant in the solution such as heavy metal ions. This technology also capable of removing organic compounds also suspended solid with depending on the size of the particles that have to be retained. Filtration techniques have various types: ultrafiltration, nanofiltration and reverse osmosis. Further research can be done for analyze further in membrane properties for extraction.

2.2.5 Adsorption Process.

The mechanism of formation hydrogen peroxide and ozone in the extraction process give higher percentage removal of pollutant. The addition of coal ash generates OH^\bullet radicals and was performing reaction between hydrogen peroxide and ozone in the solution for remove phenol as a element desired. C. S. Liu et al., (2009) found that the process by addition of ultrasonic irradiation was give higher performance and with different condition either acidic or alkaline also give their affect. The experimental result done shown 83.4% and 88.8% of phenol was degrading when coal ash added assisted by ultrasonic irradiation. The formation of hydrogen peroxide and ozone was related with the acidic or alkaline condition of solution.

Table 2.1: Summarized of Advantages and Disadvantages used different methods of removal pollutants in waste water.

Methods / Description	Advantages	Disadvantages
Catalysts - Free cations and pore zeolite opening will give affect for ion exchange occur for using different solvents extractor	Environmental friendly (M.D Loizidou and V.J Inglezakis, 2007).	Higher cost consumption.
Emulsification assisted Membrane - Performed emulsification for new interface formation and affect the cuprum (II) extraction by higher lifetime of external aqueous.	Reduce cost consumption for maintenance. (Mahdi C. et al., 2010).	Higher consumption.
Adsorption/Catalyst - Higher dosage adsorption can react as catalyst for catalyzed the extraction process by generate $\bullet\text{OH}$ radical with the present of $\text{H}_2\text{O}_2/\text{O}_3$ for degrade the pollution.	Environmental friendly (C. S. Liu et al., 2009)	Raw material difficulties to find
Solvent extraction - The ability of solvents to reduce the electric field with performs chemical reaction of ion exchange and pH affect.	Higher performance (J. S. Park et al., 2007)	Cost consumption for buy the solvent.

Table 2.1 above was shown the summarized of the method that recently used in previous researched to remove other pollutants in the wastewater. Each method that applied has own ability and strength for treatment the sample. So, different method was give different percentage of the removal pollutants.

2.3 Ultrasonic.

2.3.1 Introduction.

Ultrasonic is the sound wave that above the sound limitation from hearing human. Then, it can we use as the tools we used to perform the degradation process more easily and faster. Transducer is a device that used in ultrasonic tools to convert electrical energy to ultrasound or sound wave. The ultrasonic process is start with the emission of wavelength into the solution to form bubbles in the solution. Ultrasonic will perform sonication by applying sound energy with certain frequency to agitate the particle sample then it will speed dissolution by breaking the intermolecular molecule for further examination. This condition effectiveness is based on the large negative pressure to produce great force for penetrate the material.

Ultrasonic waves will propagated as oscillatory motion which is repetitive motion through materials: solid, liquid or gas. Effects ultrasonic with high-intensity oscillation will perform cavitation mechanism and will undergo to other process by increasing in temperature.